Bi-phasic epoxidation reaction in the absence of surfactants – integration of reaction and separation steps in micro-tubular reactors

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Abstract

This paper presents a paradigm shift with respect to the current direction of bi-phasic reactions in surfactant-free emulsions: herein, the contact area between both phases is simply sustained by the reactor design (i.e. diameter of the tubular reactor) compared to the current trend of using reversible/switchable emulsions where the addition of an external agent (e.g. bi-stable surfactant, magnetic particles, etc.) is required. In this way, temporally stable phase dispersions using micro-tubular reactors facilitate the integration of reaction and separation steps in bi-phasic systems without the need for energy-intensive downstream separation steps. In this study, we demonstrate this innovative tool in the epoxidation reaction of sunflower oil with hydrogen peroxide. Using a combination of mechanistic and kinetic studies, we demonstrate that the poor solubility of the catalytic species in the oil phase may be used advantageously, allowing ready recyclability of catalyst (and oxidant) in consecutive runs.

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Introduction

The design of chemical processes with a focus on the minimisation of energy consumption and use of materials during the separation steps is an attractive way of moderating the environmental impact in an economically beneficial manner. Thus, this strategy is defined as one of the principles of green engineering,[1]. In this context, the poor miscibility of bio-derived oily feedstocks with water presents an attractive opportunity for the integration of reaction and separation steps to facilitate catalyst recyclability and product purification. It is easy to envisage a solvent-free multi-phasic system where the reactants and/or products are immiscible in the catalytic solution in the absence of organic solvents. A classic example of this type of system is the green oxidation of organic substrates using hydrogen peroxide as green oxidant, where homogeneous tungsten-based catalysts act as oxygen mediators between phases.[2] In order to avoid mass transfer limitations, a number of phase transfer agents have been developed to ease the transfer of the catalytic species between aqueous and organic phases. Different strategies have ranged from the introduction of specific counterions to the active catalytic species[3, 4] to the incorporation of ligands to promote the phase transfer.[5] However, despite providing satisfactory rate of reactions, these strategies have a detrimental effect on the catalyst recyclability.

An alternative approach is the promotion of the reaction by increasing the liquid-liquid contact area by dispersion of one phase into the other, forming emulsified reaction systems, as demonstrated in a number of examples.[6, 7] In the majority of these cases, amphiphilic compounds, usually surfactants with hydrophilic head groups and lipophilic tails, are used to support the phase dispersion and consequently increase the interface area. However, the presence of surfactants in the interface can retard the transfer of specific compounds between phases. Although the stabilisation of a liquid-liquid interface is often a primary goal for many formulation scientists in the pharmaceutical, food and consumer products industries, it introduces an energy requirement for the post-reaction separation of phases in reactive systems. Obvious disadvantages raise when one of the phases has to be potentially recycle.

The use of solid particles such as nanocrystallites, colloidosomes and microgels are also able to stabilise phase dispersions as Pickering emulsions,[8] providing tri-phasic liquid-solid-liquid reaction systems with easy separation by the removal of the particles using classical filtration or centrifugation. Alternative approaches to facilitate the integration of the reaction and the separation steps include the use of responsive surfactants with controllable stabilities sensitive to temperature,[9, 10] pH of the solution,[11] electrical potential,[12, 13] light[14, 15] or presence of CO_2.[16] However, despite the impressive progress in the field, the use of such amphiphilic compounds (surfactants or solid particles) usually increases the carbon footprint of the overall process by increasing the energy required on downstream separation units with its obvious economic implications.

A more elegant way is the promotion of the liquid-liquid contact area by means of reactor design. Indeed, microreactors have been successfully used to produce dispersions with uniform droplet sizes by careful control of the sheer forces in different channel configurations.[17, 18] In this paper, we present the combination of mechanistic and kinetic studies for the integration of the epoxidation reaction and the catalyst separation steps using micro-volumetric reactors where phase dispersion is temporally sustained by the reactor dimensions in the absence of surfactants. At the exit of the reactor, phase separation takes place spontaneously, without any added energy input, due to the difference of densities of the phases, allowing the catalyst and/or reactants to be easily recycled in consecutive runs.

Experimental procedures

Sodium tungstate dihydrate (>99.0% purity), glacial acetic acid, hydrogen peroxide (35 wt.% aqueous solution) and sorbitan monolaurate, SPAN®20, were purchased from Sigma Aldrich and used without further purification. Sunflower seed oil (density 918 g L^{-1}) was purchased from J. Sainsbury plc. The fatty acid profile of the sunflower oil was characterised using ^{1}H NMR spectroscopic, following the methods described by Knothe and Kenar[19]. The oil consisted of a mixture of C18:2 (57.3%), C18:1 (35%) and C18:0 (7.7%), with no C18:3 detected. The average degree of unsaturated sites per molecule as n_{alkene} / $n_{triglyceride}$ was calculated as 1.496, and the concentration of double bonds in the oil as 1.55 mol L^{-1}.

Bi-phasic epoxidation reactions were carried out in a 46’ (14 m) long tubular HALAR® reactor with a 0.03” (0.76 mm) internal diameter and a total volume of 6.36 mL. The aqueous and oil phases were introduced in the reactor using two Harvard Apparatus 11 plus syringe pumps. A T- junction injection was used to disperse the aqueous phase into the oil phase by varying their relative flowrates. The aqueous phase consisted of a 3 *M* H_2O_2 solution with Na_2WO_4 catalyst concentrations varying between 0.1 and 0.4 *M*. In all cases, the Na_2WO_4:acetic acid molar ratio was constant at 0.05. Negligible epoxidation conversion was observed in the absence of Na_2WO_4 catalyst, confirming that the potential *in-situ* formation of peracetic acid in the system is not the primary oxidant specie in the reactions shown herein. The oil phase consisted of pure sunflower seed oil, except in the reactions in the presence of surfactant, SPAN®20, where the corresponding amount of surfactant (10 vol.%) was pre-dissolved in the oil. Although in the presence of surfactant the oil to aqueous volume ratio is the same than in its absence, the tryglycerides to aqueous ratio slightly lowers. However, this variation has been considered when calculating the rate of reaction. The reaction temperature was controlled by immersing the reactor in a heated paraffin bath. At the exit of the reactor, the reaction mixture was cooled in an ice/water bath where both phases spontaneously separated due to the difference in densities.

Aliquots of the reaction mixture were characterised using ^{1}H NMR spectroscopic analysis of samples of the oil phase extracted into $CDCl_3$ and dried using magnesium sulphate. The conversion of alkene to epoxide was followed by comparison of the integrated area of the alkene signals at 5.25-5.50 ppm with that of the triplet corresponding to the epoxide signal at 2.96 ppm, using the glycerol C<u>H</u> signal (4.4-4.0 ppm) as an internal standard. As the important quantity here is the number of double bonds converted to epoxides, we do not convert these values to concentration of epoxidised oil. No epoxide opening was detected under the conditions of the experiment, as verified by the absence of signals due to <u>H</u>C-OH in the region δ = 3.5-3.7 ppm (as ring opened diols are readily extracted into CDCl3 and this region of the spectrum is uncluttered by signals due to other protons, ring opening would be readily detected at levels above ca 1 %).

The overall rate of reaction was calculated using equation (1) where $C_{=,initial}$ is the initial concentration of double bonds in the oil phase (1.55 mol L^{-1}), X is the conversion, V_{oil} is the volume of the oil phase, t_R is the residence time and $V_{reactor}$ is the volume of the reactor.

$$\text{rate}\ \left(\frac{mol_{alkene}}{L \cdot min}\right) = \frac{C_{=,initial} \cdot X \cdot V_{oil}}{t_R \cdot V_{reactor}} \quad (1)$$

In the recycle studies, the oil and aqueous phases were repeatedly recycled in consecutive runs. To avoid artefacts due to the parallel decomposition of hydrogen peroxide during and between runs, the hydrogen peroxide, catalyst and acetic acid concentrations in the aqueous phase was adjusted back to its original values prior each recycle run.

The contact area between the aqueous and oil phases was measured by imaging the dispersions using a digital microcapture camera. A minimum of ten images were taken every 30 seconds, to gain an even spread at steady state operation and ensure the regularity of the dispersion. In the case of the slugs, only the front and back distorted hemispheres of the slugs were included in the contact area calculations.

Results and discussion

Continuous epoxidation of sunflower oil with hydrogen peroxide in the absence of surfactant was carried out using a tubular HALAR® flow reactor with a 0.03” internal diameter. A conventional T-junction was used to disperse the aqueous and the oil phases. The oil phase consisted of pure sunflower oil, while the aqueous solution contained the catalyst, Na_2WO_4, oxidant, H_2O_2, and acetic acid as additive to i) prevent the parallel decomposition of H_2O_2 and ii) facilitate the transfer of the active catalytic species to the oil phase.[20] Slugs of one phase in the other were formed without development of individual droplets (i.e. diameter smaller than the internal diameter of the tube) under the conditions studied. By comparison, the presence of surfactant (SPAN20, 10 vol.% oil) led to formation of individual droplets as shown in Figure 1.

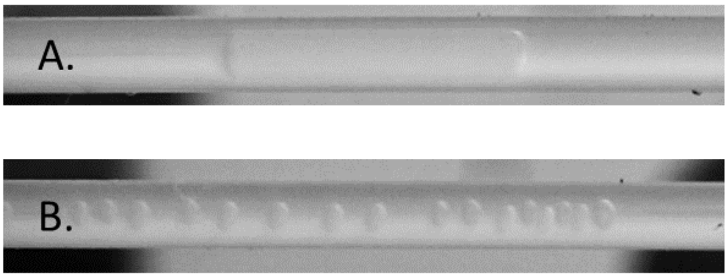

Figure 1: Formation of A. aqueous slugs in the absence of surfactant and B. individual droplets in the presence of SPAN20.

In order to provide further insight into the kinetic aspects of the system, two sets of reactions were conducted (Table 1). Initially, the concentration of catalyst (between 0.1 and 0.4 *M*) was varied, keeping the Na_2WO_4:acetic acid ratio equal to 0.05. We have recently demonstrated that increasing the Na_2WO_4:acetic acid ratio above 0.05 is detrimental, allowing the non-productive decomposition of hydrogen peroxide in the absence of phase-transfer catalysts.[20]

Table 1: Bi-phasic epoxidation of sunflower oil with hydrogen peroxide in continuous flow

Aqueous flowrate mL min^{-1}	Oil flowrate mL min^{-1}	Surfactant	$[Na_2WO_4]_{aqueous}$ / *M*	$[Na_2WO_4]_{total}$ / *M*	Rate of reaction / $mmol_{alkene}$ L^{-1} min^{-1}	Average contact area / cm^2 cm^{-3}
0.30	0.30	-	0.4	0.20	3.7	2.35
0.30	0.30	-	0.2	0.10	1.2	2.35
0.30	0.30	-	0.1	0.05	0.5	2.35
0.30	0.20	-	0.4	0.24	4.1	2.48
0.30	0.10	-	0.4	0.30	3.7	2.97
0.30	0.05	-	0.4	0.34	3.3	3.42

0.30	0.40	-	0.4	0.17	3.5	0.17
0.30	0.30	10 vol.% SPAN20	0.4	0.20	4.1	23.75

Reaction conditions: Na_2WO_4:acetic acid ratio equal to 0.05, 3 M H_2O_2, 60 °C.

Contact area between phases calculated by quantification of the average number of slugs/droplets per reactor volume

Figure 2A shows the linear relationship between the rate of reaction and the concentration of catalyst under constant conditions of flowrate, temperature and concentration of hydrogen peroxide. Interestingly, a similar rate of reaction is observed in the presence of SPAN20 under comparable conditions.

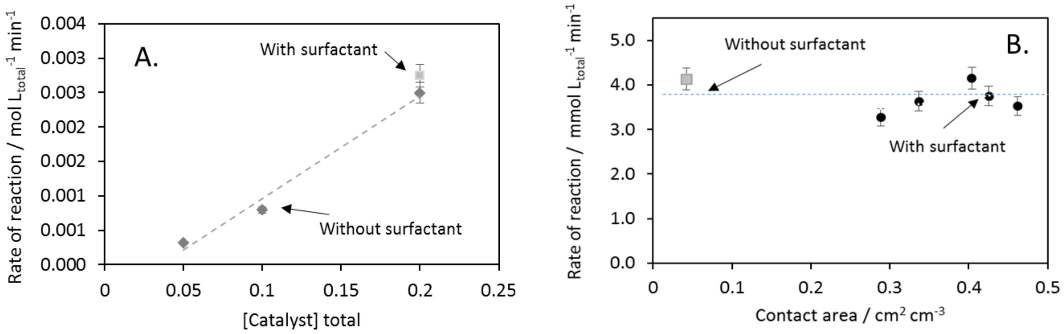

Figure 2: A. Relationship between rate of reaction and concentration of catalyst. Flowrate: 0.3 mL min^{-1} aqueous phase, 0.3 mL min^{-1} sunflower oil, Na_2WO_4:acetic acid ratio equal to 0.05, 60 °C, ♦ in the absence of surfactant and ■ with 10 vol.% SPAN20 in the oil phase and B. Relationship between rate of reaction and phase contact area 0.4 M Na_2WO_4, 8 M acetic acid, 3 M H_2O_2, 60 °C • 0.3 mL min^{-1} aqueous phase and variable sunflower oil flowrate (between 0.05 – 0.4 mL min^{-1}) in the absence of surfactant ■ 0.3 mL min^{-1} aqueous phase, 0.3 mL min^{-1} sunflower oil in addition to 10 vol.% SPAN20 in the oil phase. (The small differences of rate of reaction values is due to the differences in overall catalyst concentration at different aqueous/oil flowrate ratios despite the constant catalyst concentration in the aqueous phase).

In the second set of experiments, the contact area between both phases was varied by modifying the oil phase flowrate (between 0.05 and 0.4 mL min^{-1}) while keeping the aqueous phase flowrate constant at 0.3 mL min-1. As expected, the length of the oil slugs increased when the oil flowrate increased, thus varying the number of slugs per volume of reactor (oil/aqueous phase contact area). The rate of reaction seems to be independent of the contact area between the oil and aqueous phases, as shown in Figure 2B. A comparable rate of reaction is observed in the presence of surfactant (10 vol.% SPAN20) under the same reaction conditions, where the contact area is an order of magnitude higher than in the absence of surfactant, emphasising the independence of rate of reaction with respect to phase contact area. The rate of reaction in bi-phasic systems is independent of the contact area when any of the chemical (reaction) steps taking place either in the oil or in the aqueous phase is kinetically slower than the diffusion steps, including bulk diffusion of molecules in the oil and aqueous phase or across the phases.

Careful consideration of the different chemical and physical steps taking place in the bi-phasic system and modelling of the observed reactivity using a pseudophase kinetic model previously applied to emulsion systems[21, 22] provides some insight into the system. The different steps taking place in the bi-phasic epoxidation of sunflower oil using Na_2WO_4 as catalyst are schematically represented in Figure 3. Initially, the actual catalytic species are formed by *in-situ* oxidation of Na_2WO_4 by hydrogen peroxide. Acetic acid is believed to bind to the tungstate centre of the active catalytic species increasing the electrophilicity of the peroxo moiety[23], facilitating its physical transfer ~~of this active catalytic species~~ into the oil phase which allows the epoxidation reaction of sunflower oil to proceed in the oil phase. Finally, the reduced catalyst is transferred back into the aqueous phase to complete the catalytic cycle. (Parallel decomposition of hydrogen peroxide can take place in the aqueous phase although its rate is negligible under the Na_2WO_4: acetic acid ratios used in this study.[20])

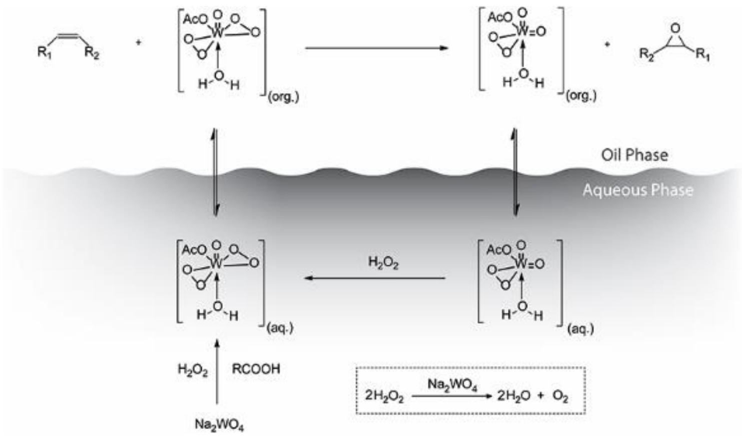

Figure 3 Schematic representation of the epoxidation of alkenes (e.g. sunflower seed oil) with hydrogen peroxide, sodium tungstate catalyst and carboxylic acids (e.g. acetic acid). The parallel decomposition of H_2O_2 is also shown. The representation of the active catalytic species follows Noyori and co-workers.[2]

The lack of surfactant in the unstabilised bi-phasic system allows simplification of the pseudophase kinetic model; only two phases (oil and aqueous) need to be considered as interface volume reduces to zero. If the overall concentration (mol L^{-1}) of active catalytic species is $[catal]_T$ and $[catal]_w$ and $[cata]_o$ are the concentrations (mol L^{-1}) of the active species in the aqueous and oil phases respectively, the partition coefficient of the active catalytic species is defined as:

$$P_o^w = \frac{[catal]_w}{[catal]_o} \qquad (2)$$

Under mass transfer control, the rate determining step is the transfer of active catalytic species across the phase boundary according to Fick's law, where the overall rate of reaction is directly proportional to the contact area between phases, as expressed in Equation (3). However, as illustrated in Figure 2B the bi-phasic system under the current conditions is not mass transfer limited, even at oil/water phase contact area values as low as 0.17 cm^2 cm^{-3}

$$rate = D_{wo}A_{wo}[[catal]_w - [catal]_o] = D_{wo}A_{wo}[P_o^w - 1] \qquad (3)$$

Under chemical control, the overall rate of reaction can be assumed to be pseudo-first order due to the excess of hydrogen peroxide in the system, defined by equation (4).

$$rate = k'_{obs}[catal]_T = k_{oil}[catal]_o \, \varphi_o = k_w[catal]_w \varphi_w \qquad (4)$$

Where k'_{obs} is the pseudo-first order rate constant, k_{oil} and k_w are the rate constants in the oil and aqueous phases and φ_o and φ_w are the oil and aqueous volume fractions respectively.

Equation (5) can be derived in terms of measurable parameters by combining equation (4) with the overall mass balance equation:

$$k'_{obs} = \frac{k_{oil}[catal]_o \, \varphi_o}{[catal]_T} = \frac{k_{oil}\varphi_o}{\varphi_o + P_o^w \varphi_w} \qquad (5)$$

And linear expression of equation (5) is shown in equation (6):

$$\frac{1}{k'_{obs}} = \frac{1}{k_{oil}} + \frac{P_o^w}{k_{oil}} \frac{\varphi_w}{\varphi_o} \qquad (6)$$

The linear relationship between $1/k'_{obs}$ and the water/oil volume ratio, shown in Figure 4, demonstrates that the kinetics of the chemical steps control the overall rate of reaction in the system. This is in agreement with the conclusions by McClements *et al.*[24] who estimated that the diffusion of molecules is not rate limiting unless there is some substantial kinetic barrier restricting their motion. Additionally, the kinetic model allows the quantification of the epoxidation first-order rate constant in the oil phase (k_{oil} = 0.086 min) and the estimation of the partition coefficient of the active catalytic species in the water and oil phases (P_o^w= 3.59). This coefficient value, within the standard range,[21] suggests that the active catalytic species formed *in-situ* by oxidation of Na_2WO_4 by hydrogen peroxide are preferentially dissolved in the aqueous phase under steady state conditions.

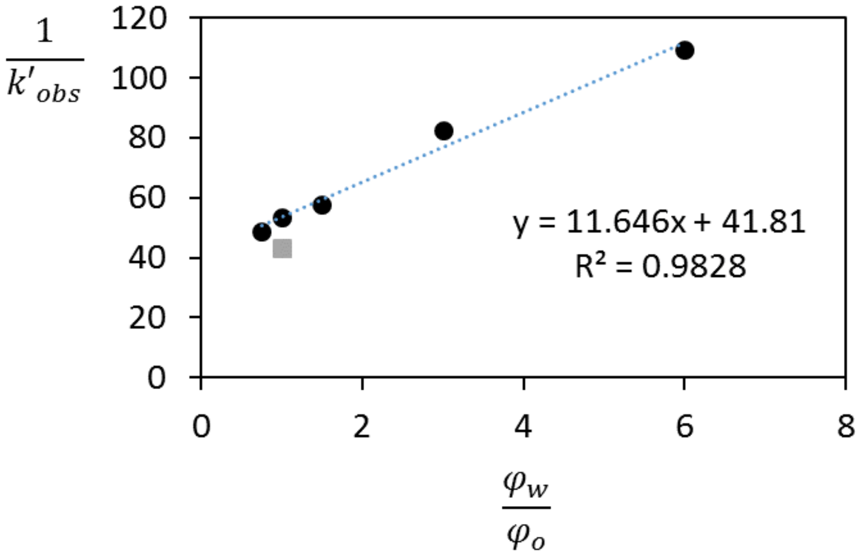

Figure 4: Linear relationship between 1/k'$_{obs}$ and the water and oil volume ratio. Reaction conditions: 0.4 M Na_2WO_4, 8 M acetic acid, 3 M H_2O_2, 60°C • 0.3 mL min^{-1} aqueous phase and variable sunflower oil flowrate (between 0.05 – 0.4 mL min^{-1}) in the absence of surfactant ■ 0.3 mL min^{-1} aqueous phase, 0.3 mL min^{-1} sunflower oil in addition to 10 vol.% SPAN20 in oil phase

The absence of surfactants in the system facilitates the phase separation at the exit of the reactor by a simple difference of densities, without any energy input. This allows the recycle of each of the phases in consecutive runs in order to reach the desired levels of conversion, greatly increasing the turn-over number (TON) of the catalyst. In this case, however, a fresh aliquot of the aqueous solution (Na_2WO_4, acetic acid and H_2O_2) is used in each recycle run in order to diminish the effect of hydrogen peroxide decomposition between runs. A linear increase of overall conversion to epoxide is observed (Figure 5) and the rate of reaction does not vary significantly (secondary y-axis, Figure 5), which is in agreement with the preferential partitioning of the active catalytic species into the aqueous phase. This avoids the increase of catalytic species in the system in consecutive runs due to their accumulation in the recycled oil phase. In this way, the lack of solubility of the catalytic species in the reaction phase (oil) is used in an advantageous manner, allowing spontaneous separation of the catalyst, so avoiding the need for downstream purification steps of the epoxidised oil. The potential mass transfer limitations are overcome by sustaining the phase dispersion by the reactor itself (e.g. tube dimension). The proposed methodology for the integration of reaction and separation steps in bi-phasic systems using unstable dispersions is applicable to (almost) any bi-phasic system, providing an attractive alternative to stable emulsions systems and reversible/switchable emulsions, negating the input of energy needed for the separation step.

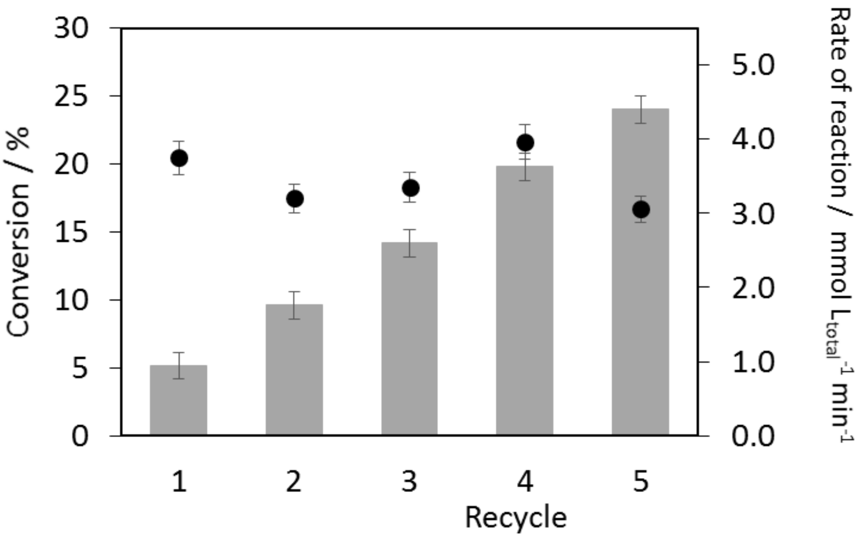

Figure 5: Sunflower oil epoxidation conversion (bars) as a function of the recycle run. • represents the rate of reaction (secondary y-axis). Reaction conditions: 0.3 mL min^{-1} aqueous phase (0.4 *M* Na_2WO_4, 8 *M* Acetic acid 3 *M* H_2O_2), 0.3 mL min^{-1} sunflower oil, 60 ^{0}C, residence time: 10.6 min

Conclusions

The epoxidation reaction of sunflower oil with an homogeneous tungsten-based catalyst, using hydrogen peroxide as green oxidant, was carried out in unstable emulsions in the absence of surfactants. The reaction and separation steps were integrated by using the reactor configuration to sustain the phase dispersion for a short period of time while the reaction take place, followed by the phase separation without any energy input. Mechanistic considerations, combined with a pseudo-phase kinetic model reveal the poor solubility of the catalytic species in the oil phase, facilitating its recyclability in consecutive runs until the desired conversion is achieved. Additionally, it also enables optimisation of hydrogen peroxide use (supporting the economic feasibility of this type of system in large-scale applications) and modulation of the degree of epoxidation of vegetable oils. The latter is important as it is seldom desirable to achieve high levels of conversion, instead these must be modulated for different applications and this system provides the flexibility to achieve this

Acknowledgments

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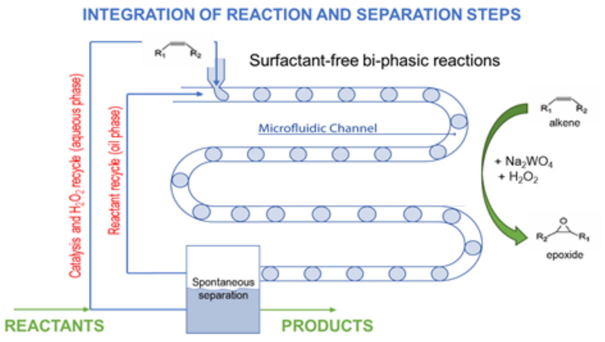

Title: Bi-phasic epoxidation reaction in the absence of surfactants – integration of reaction and separation steps in micro-tubular reactors

Authors: Laura Torrente-Murcianoa, Simon D. Bishopp, Dominic Fox and Janet L. Scott

Synopsis: Unstable emulsions sustain by micro-tubular reactors allows the integration of reaction and separation steps with minimum energy input requirements